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Surface Tension Measurement for Optimization of Flotation Control

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Abstract

In the mineral processing industry froth flotation has been widely used for ore concentration. Recently, we found that, for a particular phosphate flotation plant (Cajati-Brazil), there is a specific relation between ore separation efficiency and surface tension of the slurry with an optimum operating point that maximizes separation efficiency. In this paper we suggest on-line in-situ measurement of surface tension in the flotation cell and application of this information for process control. We propose appropriate measurement concepts and instrumentation which are suitable for the typically harsh flotation environment. Besides other measurement parameters, such as pH value, ore composition and feed rate, surface tension represents a valuable complementary process parameter which is considered to be beneficial for improvement of the flotation control. We suggest using this additional information as input for a model predictive control system (MPC), which was developed by ABB and successfully applied in a zinc flotation plant (Garpenberg, Sweden). Accurate knowledge of the relation between surface tension of the slurry and the ore separation efficiency in combination with a refinement of the physical model provides the basis for an improved MPC. A system on this basis may lead to a more profitable process regarding ore recovery or ore grade.

Keywords: *:* phosphate beneficiation; ore separation; flotation; surface tension; tensiometer; process control;

1. Introduction

Concentrates of apatite, assaying P_2O_5 content greater than 30%, are required for the manufacture of phosphoric acid, fertilizers and many other chemical products. Apatite is found in nature in both sedimentary, as it occurs in Morocco, USA and China, and also in igneous deposits, as it happens predominantly in Brazil, South Africa, Russia and Canada. In both kinds of ore, the main gangue minerals associated with apatite are carbonates (dolomite and calcite), silicates and oxides [1]. Although several processes have been used to separate apatite from gangue minerals around the world, it is not possible to ignore the major role played by froth flotation which responds for more than 60% of the world's marketable phosphate production [2].

Froth flotation is a surface chemistry-based unit operation that involves the capture of hydrophobic particles by air bubbles in aqueous slurry, followed by levitation and collection in a froth layer. Conversely, because hydrophilic particles do not adhere to air bubbles, they are likely to sink and go to the underflow of the flotation cell [3]. When P-bearing minerals (as apatite and francolite) are rendered hydrophobic and float, the process is named direct flotation and the yielded

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froth is the phosphate concentrate. *Mutatis mutandis*, reverse flotation occurs whenever particles of gangue minerals (as quartz and carbonates) are rendered hydrophobic and float. In this case, the yielded froth constitutes the tailings, whereas the underflow is the phosphate concentrate.

The key for success of apatite-gangue separation via froth flotation is the efficient control of wetting phenomena which, in turn, determines the selectivity of the process. The regulation of the interaction of minerals (apatite and gangue) with water molecules (hydrophilic nature) and also with air bubbles (hydrophobic nature) is achieved upon the addition of chemical reagents (collectors, modifiers and frothers) to the flotation pulp. Adsorption of chemical reagents onto interfaces is the most effective approach to promote the hydrophobicity of the mineral which is desired to float and also the reinforcement of the wettability by water of the minerals which are not desired to float. Therefore, an efficient separation apatite-gangue relies on the judicious use of chemical reagents for controlling the characteristics of solid-solution, gas-solution, and gas-solid interfaces, as well as the chemistry of the aqueous solution [3].

When the dosage of flotation reagents is adequate to promote a selective apatite-gangue separation, the content of P2O5 and impurities (MgO, SiO_2, Fe_2O_3 and Al_2O_3) in the apatite concentrate lay within an acceptable range posed by market specifications, for instance: P_2O_5>35%, MgO<1% and Fe_2O_3+Al_2O_3<3%. However, when collector dosage, for instance, is inappropriate to promote a selective separation, the information on the quality of the concentrate may take a length of time that is long enough to allow an industrial process to yield hundreds (even thousands) of tons of concentrate which do not meet market specifications. The purpose of this work is to propose the measurement of surface tension of flotation solution aiming at accelerating the decision-making process on increasing or decreasing the collector dosage in order to achieve the best possible efficiency of the separation between apatite and gangue minerals via froth flotation.

2. Background

Long-chain collectors, such as fatty acids, alkyl sarcosinates and sulfosuccinates, commonly used in phosphate flotation plants are capable of adsorbing onto apatite/water interface, turning its naturally hydrophilic character hydrophobic. A linear relationship between the contact angle of igneous apatite from Ipira-Brazil and the flotation recovery with sodium oleate (0 to 75 mg/L) is reported in [4]. As expected, the higher the contact angle, the higher the flotation response. On the other hand, long-chain collectors are capable of adsorbing not solely onto the apatite/water interface, but also onto the air/solution interface. This way, they are able to lower the magnitude of surface tension of the flotation solution γ_{LV}.

Typical values of γ_{LV} at the rougher flotation stage at a particular Brazilian industrial plant located in Cajati-Brazil were reported in [5]. The reported values of γ_{LV} lay in the range of 36-39 mN/m, whereas at the cleaner stage, γ_{LV} is slightly higher (38 mN/m $\leq \gamma_{LV} \leq$ 40 mN/m). Because the value of contact angle θ of a solid depends greatly on the magnitude of the surface tension of the solution γ_{LV} in which the solid is immersed, the lower the magnitude of γ_{LV}, the lower the contact angle of the mineral particles [6].

Particles of Ca-bearing gangue minerals, such as dolomite and calcite, interact strongly with long-chain collectors, such as alkyl sarcosinate [7] and fatty acid soaps [8]. In Brazilian flotation plants, although a modifying agent (starch) has been used to increase the selectivity of the separation process, high levels of MgO and CaO from carbonate gangue minerals or MgO from silicates (phlogopite, olivine and pyroxene) are found in the current apatite concentrates. If particles of gangue minerals, either carbonates or silicates, float together with apatite by means of true flotation (the result of successful particle-bubble collision, adhesion and levitation until the froth layer), they were certainly poorly wetted by flotation solution containing reagents ($\theta > 0°$). Based on this rationale, it is reasonable to expect that there is any particular value of γ_{LV} or a range of values, under which particles of apatite are less wetted by flotation solution than gangue minerals. Actually, as depicted in Figure 1, results reported in [5] indicate that, at a particular Brazilian industrial plant (Cajati-SP), surface tension of flotation solution γ_{LV} can be modulated by collector dosage, and its magnitude can provide guidance to practitioners to make decision on collector dosage to achieve a desired value of $\gamma_{LV} \approx$51mN/m which promotes the best selectivity of the separation apatite/gangue. Thus, not only the separation efficiency is optimized but also the collector consumption and disposal effort.

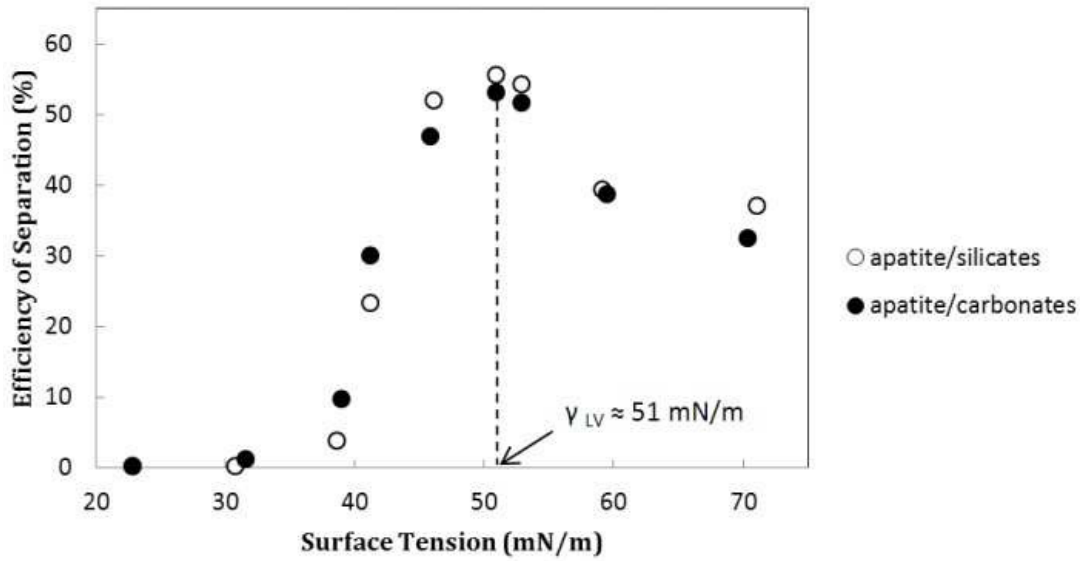

Fig. 1. Plot of separation efficiency versus surface tension of flotation solution for apatite/silicate and apatite/carbonate systems [5]

In order to identify suitable instruments to carry out on-line reliable measurements of γ_{LV} at industrial circuits, ABB is collaborating with the Mineral Processing Group of the University of Sao Paulo-Brazil, aiming at developing and testing a device to conduct on-line measurements of γ_{LV} in industrial flotation circuits.

3. Surface tension measurement methods

For many industrial processes, such as cleaning, de-inking, plastics flotation and mineral flotation, it is vital to understand the surface chemistry in the process liquid [9-11]. Depending on the process target surface active substances (surfactants) can be necessary or problematic for the process. In this context the surface tension represents an important parameter which can be used as an indicator for the presence and concentration of specific surface active substances in the liquid. Consequently in flotation processes the surface tension is a parameter which should be monitored and controlled. By continuously monitoring this quantity the liquid properties and thus the process can be better understood and the information can be used to control the concentration of different substances in the liquid without time delay. Particularly on-line surface tension measurements are very promising for monitoring mineral flotation and for controlling surfactant (collector, frother and modifier) performance in flotation processes as reported by [5,10,12].

There are various methods to measure surface tension, among them the most popular are the following: the Wilhelmy plate method and Du Noüy ring method. Both are based on force measurement whereas the value is acquired in quasi thermodynamic equilibrium (static surface tension measurement). Two other static methods are the spinning drop method and the pendent drop method. Methods which provide the dynamic surface tension are e.g. the drop volume method, the maximum bubble pressure method, the oscillating jet and the inclined plate method.

For the control of phosphate mineral flotation we propose the method of maximum bubble pressure [13]. The principle of this method is described in the following (Figure 2):

Typically an inert gas, such as nitrogen is passed through a small capillary into the fluid. At the orifice of the capillary (the gas/liquid interface) the formation of a bubble starts. As the bubble grows, the bubble pressure increases to a maximum value (pressure is inversely proportional to the radius of curvature of the bubble). At this point the bubble diameter is equal to the orifice diameter. The time of this growth phase is referred to as the surface age. Beyond this point the bubble grows rapidly (fast pressure drop) and finally detaches from the capillary and a new bubble formation cycle will start. The time period from maximum pressure to the start of a new cycle is called dead time.

The relation of bubble pressure and surface tension in these capillary type instruments is given by the following equation [13]:

$$p(t) = \frac{2\gamma}{r(t)} + \rho g h + \Delta p \qquad (1)$$

where γ is the surface tension of the liquid, r is the bubble curvature radius, ρ is the density of the liquid, g is the acceleration of gravity, h is the depth the capillary is immersed into the liquid, and Δp is a correction value attributed to hydrodynamic effects. The first expression on the right side of eq.1 is the key to our measurement. The two latter expressions are assumed to be stable over time. Currently developed and commercialized tensiometers monitor the pressure difference over the bubble life time and take the difference between lowest and highest pressure. This value is then a measure of surface tension. There are also more sophisticated devices using two different capillaries with different orifice size. Here the difference of the two different pressure maxima are evaluated which provides a highly accurate signal that is directly proportional to the surface tension.

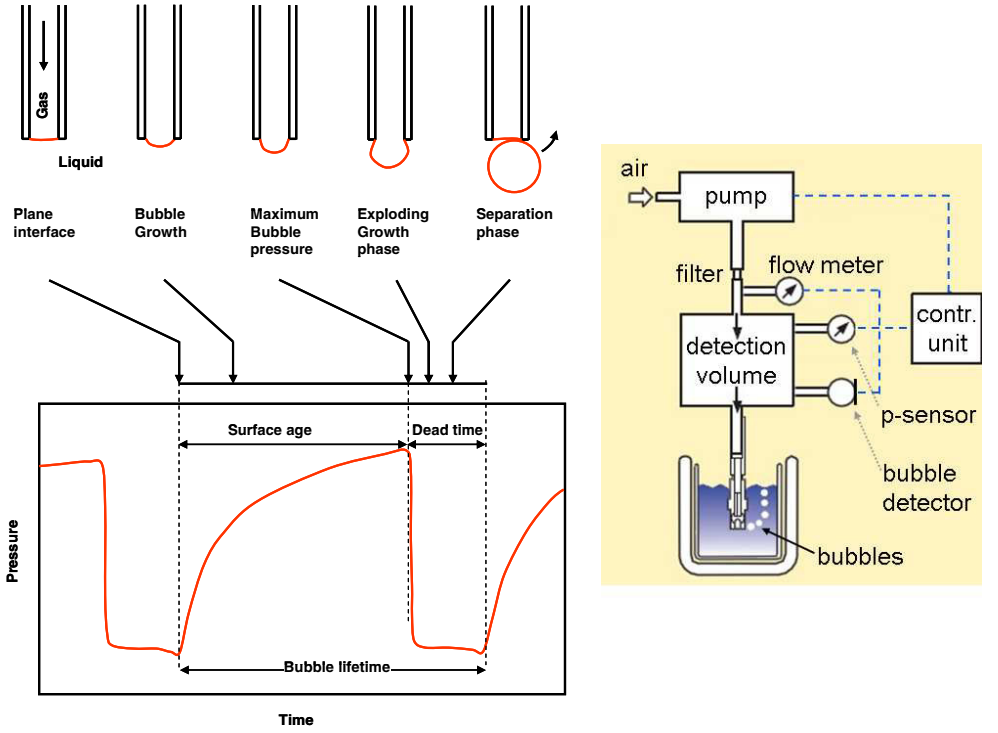

Fig. 2. Principle of dynamic surface tension measurement using the maximum bubble pressure method. (Top left) Capillary with various bubble sizes for various stages of the bubble formation process [12]; (Bottom left) Time course of pressure during bubble formation and separation; (Right) Schematic illustration of basic bubble pressure tensiometer using the Fainerman method [13].

The maximum bubble pressure method is a well-established method [14] and we believe that it is particularly suited for in-situ measurement in flotation cells because of the following advantages:

- Tensiometers can be used for continuous on-line or at-line measurement, since the measurement is done directly in the bulk liquid. Can be inserted in tanks or flow-through pipes. Immune to fluctuating liquid levels. Immune to air/liquid interface turbulence by shielding the capillaries.
- Pressure measurement allows to separate process liquid from sensor element. Pressure transducer can be far away from the liquid. No extraction of sample needed. No manual laboratory work required.
- Many sub-processes in flotation which are important in the interpretation of surfactant behavior occur on short time scales [12,15]. The maximum bubble pressure method can address these time scales. A wide range of time response can be adjusted (from milliseconds to 10 s).
- Short response times allow the monitoring of dynamic processes and fast process control (automated feedback regulation possible).
- The bubble pressure method is unaffected by surface foam or surface contamination since the measurements are made in the bulk fluid.
- Compensation of cross sensitivity effects (e.g., by pressure, temperature and viscosity changes) is possible (see section below).

4. Tensiometer instrument for harsh environment

The continuous in-situ measurement of surface tension of process liquids in industrial environment is not straightforward. Most surface tensiometers, such as Wilhelmy plate or Du Noüy ring tensiometers, are non-robust, susceptible devices just suited for laboratory analysis but not appropriate for direct application in the process. However, there are a few companies which offer analyzer instruments for on-line in-situ application, e.g., for industrial cleaning processes in semiconductor or automotive industry [9]. Another application is de-inking flotation in paper industry for which on-line monitoring devices are evaluated and discussed in [10].

Among the above discussed methods to measure surface tension, one of the most suited ones for application in the harsh mineral flotation environment is the maximum bubble pressure method. However, for direct in-situ measurements one has to account for some challenges which require specific physical provisions and compensation concepts that are outlined in the following:

- Pressure: Pressure changes in the bulk liquid, e.g., caused by fluctuating fluid levels. This effect can be compensated by using an instrument with two capillaries of different orifice diameter, a so-called differential maximum bubble tensiometer [10,16]. Such a device is commercialized by the company Sensadyne (Figure 3).
- Temperature: The surface tension is temperature dependent (typically for aqueous solutions: $d\gamma/dT \approx -0.14$ (mN/m)/K, (source: http://en.wikipedia.org/wiki/Surface_tension, 16.08.2012)). If one or more temperature sensors are added to the sensor system thermal variations in the liquid can be monitored and compensated for.
- Viscosity: If the viscosity of the liquid increases the hydrodynamic resistance of the fluid against the bubble increases significantly. In order to make the surface tension value independent of viscosity effects the ratio of the bubble rates through the two capillaries can be set in an optimum way. Details of this compensation are described in [15,16]. Alternatively, one could measure the viscosity using an additional sensor and use this signal for compensation (like for the temperature compensation).
- Flow of the liquid/slurry. Shearing or turbulence effects from flow or mixing of the fluid in the vessel can have an adverse effect on the bubble formation and detachment process. This can be mitigated by mechanical means, e.g., a porous basket placed in front of the capillaries or by doing the measurement in a by-pass where the flow is buffered.
- Contamination: Careful choice of probe material and orifice size is important to mitigate problems of coating and plugging of the probes. Stainless steel probes (surface energy: 30-40 mN/m) may be the best choice since they are robust, non-wetting to most coatings and can be produced with a high surface smoothness [15].
- Plugging: Particularly for applications with high solids content plugging of the capillaries is an issue. Under normal operating conditions a flowing gas permanently leaves the orifice of the capillary and plugging should not occur. However, for probe insertion or other manipulations purging of the probes with a high gas flow is an appropriate means to prevent plugging. Purging can also be used to unplug the probes once they should be plugged under normal operating conditions [16].

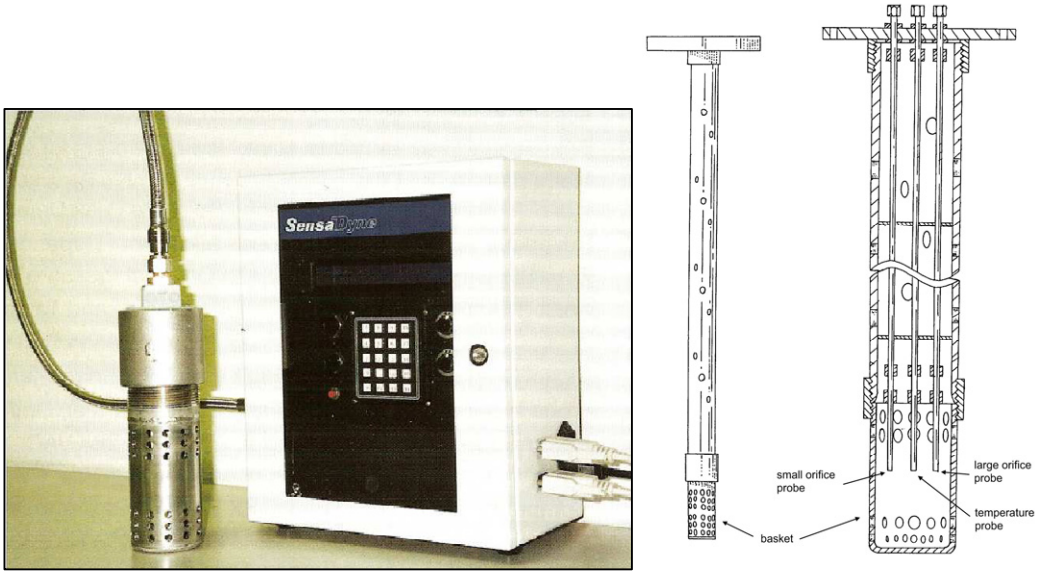

Fig. 3. Surface tensiometer for harsh industrial application from company Sensadyne. (Left) Photo of entire system; (Right) sketch of the sensor probe [16]

Since the mixing of the slurry in the flotation cell could result in a non-homogeneous distribution of particles, water and surfactants, it could be beneficial to install more than one sensor system (measuring dynamic surface tension, temperature, viscosity, pH, etc.). The advantage of placing several sensor systems of the same kind at different locations results in a better picture of what is ongoing in the vessel. This procedure allows for averaging the signals and thus for a more efficient feedback control.

5. Control optimization using model predictive control

ABB has developed a control strategy for a flotation circuit based on model predictive control (MPC) using mixed-logical dynamical systems and tested it in a zinc flotation circuit as described in [17]. The objective was to maximize the production value or yield by making optimal use of the available circuit instrumentation, i.e. actuators, sensors and low-level control loops. In the above paper, a first-principles model based on physical insight was used. As only limited knowledge about the pulp phase of the cell was available, the pulp model was restricted to volume and mass conservation, and assumed perfect mixing.

In general, for controlling a froth flotation plant only limited in-situ measurement information about the surface chemistry of the solid/liquid mixture is available. The lack of knowledge about the surface chemistry does not allow the operation and control of the plant at its optimum efficiency. However, by using further input parameters such as surface tension of the slurry and by concomitant extension and upgrade of the model the lifetime and profitability of the plant could be significantly increased.

MPC requires three to four main ingredients: a dynamical model of the process, measurements or estimates of the internal state variables (such as composition of pulp phase in each cell), an objective function to be optimized, and possibly constraints. Typically, control performance increases with the accuracy of the process model. However, this comes at the cost of higher instrumentation requirements because process model complexity and sensor types, numbers and positioning must match.

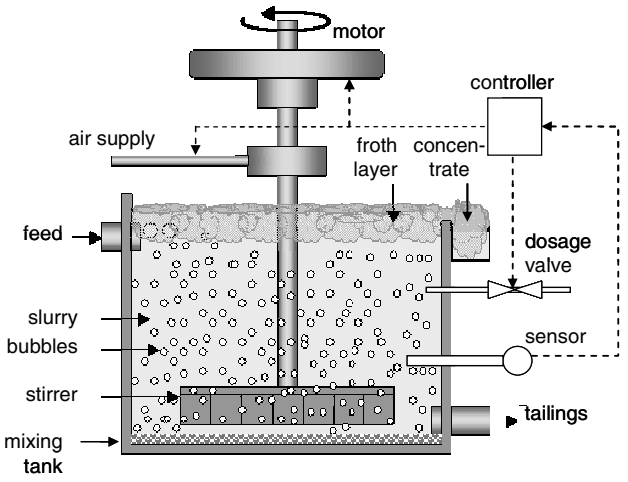

Fig. 4. Froth flotation cell with sensor, actuators and control system. The control system is fed by surface tension sensor information and finally controls actuators in the flotation cell to improve separation efficiency

Here we propose a system for controlling a froth flotation process comprising a sensor instrument for measuring continually the surface tension of the pulp and on the other hand a controller for controlling the flotation process based on a model of the flotation circuit. A schematic illustration of the flotation control setup is shown in Figure 4. The surface tension represents exemplary additional information about the surface chemistry in the flotation process, and as such enables a refinement of a pulp model used by MPC for control of the flotation process. Measuring the surface tension continually or repeatedly (e.g. every few minutes) and directly in the flotation cell or in a by-pass of the flotation cell produces valuable real-time measurement samples as a basis for future process control actions. In conjunction with various other sensor signals, control actions or set-points for the manipulated variables such as air flow rate, froth layer level and thickness, and addition of chemicals are determined. The resulting parameters are further used to deduce one or more values which are necessary to actively control the process maintaining or improving its efficiency. A potential control action could be the addition of controlled dosage of chemicals adjusting the surface tension of the flotation bath.

6. Conclusions and outlook

We have found indications that phosphate beneficiation for the flotation plant in Cajati-Brazil can be significantly improved if the surface tension is kept at its optimum value, e.g., by collector dosage control. Suitable instruments to acquire the information which is needed for control decisions are available and we propose to combine these measurement systems with a model based optimizer which runs the flotation circuit in the most profitable way. The proof of principle of these combined instrument-controller system will be demonstrated in ongoing bench-scale flotation experiments.

References

[1] Henchiri, A.A. (1993). Contribution to carbonates-phosphate separation by flotation technique. In: El Shall, H.; Moudgil, B.; M.; Wiegel, R. Beneficiation of phosphates: Advances in research and practice. SME, Littleton, p. 226-230.
[2] Abouzeid, A.M. (2008). Physical and thermal treatment of phosphate ores – an overview. International Journal of Mineral Processing, 85, p. 59-84.
[3] Urbina, R.H. (2003). Recent developments and advances in formulations and applications of chemical reagents in froth flotation. Mineral Processing & Extractive Metall. Review., 24, p.139-182.
[4] Martins, M.; Leal Filho, L.S. (2007). Medida de angulo de contato de particulas de apatita pelo metodo de ascensao capilar. VII Meeting of Southern Hemisphere on Mineral Technology/ XXII Encontro Nacional de Tratamento de Minérios e Metalurgia Extrativa (proceedings). UFOP/UFMG/CDTN, Ouro Preto-Brazil, p. 381-388 (in Portuguese).
[5] Martins, M. (2009). Molhabilidade da apatita e sua influência na flotação. Doctoral thesis. University of São Paulo, São Paulo, 119pp.
[6] Zisman, W.A. (1964). Relation of the equilibrium contact angle to liquid and solid constitution. Contact Angle, Wettability and Adhesion, F.M. Fowkes, ed., American Chemical Society. Washington, p. 1-51.
[7] Schroeder, H. (1986). Untersuchungen zur Adsorption von Ampholyttensiden und deren Mischungen mit einem nichtionogenen, polar-unpolaren Tensid auf Apatit und Scheelit. Doctoral thesis, University of Clausthal, Clausthal, 118 pp. (in German).
[8] Finkelstein, N.P. (1989). Review of the interactions in flotation of sparingly soluble calcium minerals with anionic collectors. Transactions of the Institute of Mining and Metallurgy, Section C, 9, p. 157-178.
[9] Schuemann, D. (2009). Controlled Cleaning by Measuring Surfactant Concentration, Metal Finishing, 107, pp. 25-30.

[10] Pugh, R.J. (2001). Dynamic surface tension measurement in mineral flotation and de-inking flotation systems and the development of the on line dynamic surface tension detector (DSTD), Minerals Engineering, 14, pp. 1019-1031.
[11] Kirjavainen V., Lehto H., Heiskanen K. (2003). Study on the flotation behaviour of low energy materials at low surface tensions. Minerals Engineering, 16, pp.1193-1196.
[12] Comley, B.A., Harris, P.J., Bradshaw, D.J., Harris, M.C. (2002). Frother characterisation using dynamic surface tension measurements, Int. J. Miner. Process., 64, pp. 81-100
[13] Fainerman, V.B.; Miller R.; Joos P. (1994)., The measurement of dynamic surface tension by the maximum bubble pressure method, Colloid & Polymer Science, 272, pp. 731-739.
[14] Fainerman, V.B.; Kazakov, V.N.; Lylyk S.V.; Makievski, A.V.; Miller R. (2004). Dynamic surface tension measurements of surfactant solutions using the maximum bubble pressure method – limits of applicability, Colloids and Surfaces A: Physiocem. Eng. Aspects, 250, p.97-102
[15] Janule, V.P. (2005). The dynamics of surface tension. European Coatings Journal, No.7-8, p.24-27
[16] Christensen, T.C., Teichmann, A.F., Janule, V.P. (1995). Surface tension measurement in a pressurized environment, United States Patent 6085577.
[17] Gaulocher, S.; Gallestey, E.; Lindvall, H. (2008) Advanced process control of a froth flotation circuit. Vth International Mineral Processing Seminar (proceedings). Procemin2008, Santiago-Chile, p. 327-337.